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COMPLETE SPECIFICATION

Reduction of Combustion Chamber Deposits in Gasoline Engines

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the operation of internal combustion engines and more particularly relates to the use in gasoline engines of novel scavenger agents adapted to reduce the adverse effects of combustion chamber deposits caused by combustion of gasoline containing metal-containing antiknock agents. In a preferred embodiment, the invention relates to gasolines containing mixtures of lead antiknock agents and mercury-containing additives effective for controlling the octane requirement of gasoline engines by reducing surface ignition, spark plug fouling and related difficulties attributable to the formation of deposits in the combustion chambers of the engines.

The adverse effects encountered as a result of the formation of deposits in the combustion chambers of gasoline engines operated upon fuels containing metallic antiknock agents have assumed increasing importance in recent years. This has come about primarily as a result of the increase in the compression ratios used in passenger car and truck engines. Studies have shown that combustion difficulties attributable to deposit formation are much more pronounced in late model engines having compression ratios in excess of about 9·5 to 1 than in earlier models.

Deposits formed when metallic antiknock agents are used in gasolines interfere with the normal combustion process taking place in the engine in at least three ways: (1) Compounds of low electrical resistance formed on spark plug insulators cause the plugs to misfire during some cycles and thus produce rough operation and loss of power; (2) by coating surfaces within the combustion chamber with materials of low thermal conductivity, the deposits cause an increase in the temperature of the last portion of the fuel-air mixture to burn such that this part of the mixture ignites spontaneously and the phenomenon known as spark knock occurs; and (3) by glowing hot or by catching on fire themselves, the deposits ignite the fuel-air mixture either before or after the spark plug fires, producing a type of abnormal combustion known as surface ignition.

Spark plug fouling, spark knock and surface ignition are encountered with the use of lead, iron, nickel, manganese and other metallic antiknock agents in gasoline. They are typically prevalent in engines operated on gasolines containing tetraethyl lead, tetramethyl lead, dimethyldiethyl lead and similar alkyl lead antiknock agents. Generally in the past, some relief from these combustion problems resulting from deposits in the combustion chamber has been obtained by using the antiknock agents in conjunction with halogen-containing scavengers and, more recently, with auxiliary scavenger agents, for example, certain phosphorus compounds; but despite this, the problems persist. Moreover, the excessive use of auxiliary scavengers reduces the life of the exhaust valves in engines in which they are used and depreciates the octane quality of the fuels to which they are added. For these reasons, such auxiliary scavenger agents have not proved wholly satisfactory.

The present invention provides a new class of scavenger agents for use in conjunction with gasolines containing metallic antiknock additives which greatly reduce the difficulties encountered with such gasolines as a result of the formation of combustion chamber deposits.

In accordance with the present invention, it has now been found that the inclusion, in the combustion chambers of gasoline engines operated upon fuels containing such antiknock

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Price 25p

agents, of certain small quantities of mercury-containing scavenger agents results in a reduction in the amount of deposits formed and in a modification of the character of the deposits that are formed such that difficulties attributed to the formation of deposits in the past are largely obviated.

The present invention comprises a method for preventing the formation of adherent deposits in the combustion chambers of a gasoline engine operated on a fuel containing a metal-containing antiknock agent which comprises introducing into the combustion chambers of the engine a mercury-containing substance in proportions sufficient to provide up to 2·0 gms. of mercury per gallon of gasoline burned.

The invention also comprises a gasoline composition comprising a lead alkyl anti-knock agent in proportions of from 1·0 to 6·0 c.cs per gallon, and from 0·5 to 3·0 theories of a halohydrocarbon scavenger agent and a mercury alkyl compound, wherein the alkyl groups contain from 1 to 8 carbon atoms in proportions sufficient to provide up to 2·0 gms. of mercury per gallon of gasoline.

The exact mechanisms whereby the mercury-containing scavenger agents act to reduce the adverse effects of combustion chamber deposits in gasoline engines are not fully understood. Studies have suggested, however, that the action of the agents may involve a combination of at least three separate effects which may vary in the extent to which they occur, depending upon the nature of the deposits present in the combustion chamber and upon the engine operating conditions. The first of these mechanisms, and the one which seems most likely to predominate, occurs due to the presence of atomic mercury behind the flame front as combustion takes place. The mercury atoms tend to cause a reduction in free radical formation, to effect some slowing down of high fugacity gaseous material, and to inhibit the polymerization of unsaturated hydrocarbons formed as a result of cracking reactions. A second mechanism involves the mechanical action of elemental mercury on the deposits. Mercury has the ability to diffuse and amalgamate through the metallic surfaces of the combustion chamber, causing the deposits to flake off the surfaces in very thin layers. The third mechanism involves the action of mercury and certain mercury compounds on the crystalline structure of the deposits as they are formed. Mercury halides produced by the reaction of mercury atoms with halogen atoms present in the combustion gases, for example, co-crystallize with other metallic halides formed in the combustion chamber and inhibit their crystal growth or render them less adherent to surfaces within the combustion chamber. In addition to these mechanisms, other phenomena not yet observed which render the presence of mercury during combustion particularly desirable from the standpoint of reducing combustion chamber deposits may well be involved.

As suggested by the foregoing, studies have indicated that a wide variety of mercury-containing materials may be employed as scavenger agents in accordance with the invention, including both organic and inorganic mercury compounds. In general, compounds comprising mercury in combination with organic radicals which impart oil- or gasoline-solubility and adequate volatility to the compound are preferred. Specific examples of such mercury compounds include mercury alkylides such as mercurymethide, mercury ethide, dipropyl mercury, diisopropyl mercury, di-n-butyl mercury, diamyl mercury, methyl propyl mercury, ethyl butyl mercury, dihexyl mercury, and didecyl mercury . The foregoing compounds have desirably low melting points. Mercury arylides such as dibenzyl mercury, diphenyl mercury, ditolyl mercury, and dixylenyl mercury have relatively high melting points but may be used in relatively low concentrations in gasoline. Mercury alkenyls can also be used, for example diallyl mercury, dipentenyl mercury, and allyl pentenyl mercury. Less volatile organic compounds of mercury are mercury acetylides such as mercury propylacetylide; mercury salts of aliphatic acids such as mercury acetate, mercury acrylate, mercury butyrate, mercury linoleate, mercury oleate, and mercury stearate, mercury xanthates, for example, mercury ethyl xanthate; mercury diazoates; mercury diazotates; mercury carbamates; mercury salts of thioacids; mercury salts of sulfinic acids; and mercury nitroslys. The mercury-containing scavenger agents utilized may contain, in addition to mercury, other functional groups or atoms such as halogen atoms, and hydroxyl groups. The relatively non-volatile compounds of mercury are preferably used in leaded gasoline for the operation of internal combustion engines with direct injection rather than carburetion of the gasoline.

Inorganic mercury salts may also be used provided that they have been suitably solubilized, complexed or dispersed so as to give solutions or stable dispersions of the mercury-containing salt in the gasoline. Such salts include mercuric chloride, mercuric bromide iodide (HgBrI) and mercuric phosphate.

The mercury-containing scavenger agents which are used to control the adverse effects of combustion chamber deposits in gasoline engines are preferably introduced into the engine combustion chambers by including them in the leaded gasoline upon which the engine is operated. In some circumstances, the beneficial effect of mercury compounds in the combustion chamber may be achieved in lesser degree by including them in the lubricating oil. For example, a non-volatile mercury compound like mercury naphthenate may be

added to the lubricating oil to supplement the action of a volatile compound like mercury dibutyl in the leaded gasoline. The exact amount of scavenger employed will, of course, depend upon the method of introduction which is used, upon the particular mercury compound utilized and upon the metallic antiknock present in the gasoline upon which the engine is operated. The octane requirement is measured in terms of the octane number of gasoline required to give "noise-free" operation the noise being that due to either spark-knock or surface ignition. The scavenger agents are used in concentrations sufficient to provide for the introduction into the combustion chambers of up to 2·0 grams of mercury per gallon of gasoline burned. Concentrations which will provide between about 0·0015 and about 1·5 grams of mercury per gallon of fuel consumed are useful for the purpose of the present invention; while amounts which will provide between about 0·01 and about 1·0 gram of mercury per gallon of gasoline burned are particularly effective and are preferred for use in accordance with the present invention.

For incorporation into gasolines, the mercury alkylides having alkyl groups of from 1 to about 8 carbon atoms in length are preferred scavenger agents because of their desirable volatility and solubility properties and their relatively low cost. Mercury alkylides containing a total of from about 4 to about 12 carbon atoms per molecule are particularly effective and are especially preferred.

The gasolines in which the mercury-containing additives of the invention may be employed are conventional gasolines marketed for use in internal combustion engines operating upon the Otto cycle. Such gasolines are supplied in a number of grades depending upon the particular service for which they are intended. The most general classifications applied to such fuels are those of motor gasolines and aviation gasolines. Motor gasolines are defined by ASTM Specification D-439-56T and are designated as Type A, Type B or Type C, depending upon the particular service for which they are to be used. Such fuels consist of mixtures of hydrocarbons of various types, including aromatics, olefins, paraffins, isoparaffins, naphthenes, and, in some cases, diolefins, derived from petroleum by refining processes such as fractional distillation, thermal cracking, catalytic cracking, hydroforming, alkylation, isomerization, and solvent extraction. Motor gasolines normally boil between about 80°F. and about 450°F. when tested by ASTM Method D-86. Their vapor pressures as determined by ASTM Method D-323 vary, depending on the season of the year during which they are to be used, from about 7 to about 15 lbs. psi at 100°F. Their octane numbers as determined by ASTM Method D-908 may range from about 83 to about 105 or higher. Aviation gasolines are prepared by blending of constituents similar to those found in motor gasolines but in general have somewhat narrower boiling ranges between 100°F. and 330°F. and somewhat more rigid specifications than do motor gasolines. Specifications for aviation gasolines are set forth in U.S. Military Specification MIL-F-5572.

As pointed out heretofore, the mercury-containing additives used in accordance with the invention may be employed in gasolines containing tetraethyl lead, tetramethyl lead, dimethyldiethyl lead, trimethylpropyl lead and similar alkyl lead antiknock additives. Such lead antiknock agents are always employed in conjunction with halogenated scavenger agents. The mercury-containing scavengers of the invention may be used in conjunction with these conventional scavengers.

Halogenated hydrocarbon compounds suitable for use as scavenger agents in gasolines containing lead antiknock agents are, in general, those boiling within the range between about 50°C and about 250°C. Examples of such scavenger agents include ethylene dichloride; ethylene dibromide; chlorobromomethane; tetrabromoacetylene; trichloroethylene; propylenedibromide; carbon tetrachloride; 2-chloro-2,3-dibromobutane; 1,2,3-tribromopropane; hexachloropropylene; chlorocyclopentane; trichlorocyclopentane; bromoxylene; 1,4-dibromobutane; 1,4-dichloropentane; β, β′-dichlorodiethyl ether; trichlorobenzene; dibromotoluene; 1-phenyl-1-bromoethane; ethyl-α-chloropropionate; ethyl-α-bromoacetate; diethyl-dibromomalonate; 1,1-dichloro-1-nitroethane; 2-chloro-4-nitropentane; and 1-bromo-3-hydroxybutane. Mixtures of the above and similar halogenated compounds may also be employed. Ethylene dibromide, ethylene dichloride and mixtures thereof are particularly effective as scavenger agents for alkyl lead antiknock compounds and are generally used therewith.

Halogenated scavenger agents such as those set forth above are normally employed in gasolines containing lead antiknock agents in concentrations ranging from about 0·5 to about 3·0 theories, one theory being the amount of scavenger stoichiometrically equivalent to the lead in the gasoline. One theory of ethylene dichloride, for example, is the amount of the scavenger required to provide sufficient chlorine atoms to react stoichiometrically with all of the lead in the gasoline to form lead chloride. In gasolines containing tetraethyl lead and similar alkyl lead antiknock agents, it is generally preferred to use from about 0·8 to about 1·5 theories of ethylene dibromide if a single scavenger agent is to be employed, or from about 0·8 to about 1·5 theories of ethylene dichloride and from about 0·3 to about 0·8 theories of ethylene dibromide if a mixed scavenger agent is used.

The preferred antiknock composition is Ethyl Fluid containing tetraethyl lead and

halide scavenging agents, particularly ethylene dichloride and/or ethylene dibromide. The Ethyl Fluid is generally used in gasoline to provide concentrations of tetraethyl lead between 1 cc. per gallon and 3 cc. per gallon in motor gasoline and between 3 cc. per gallon and 6 cc. per gallon in aviation gasoline. For the purpose of the present invention, the ratio by weight of the metal in the antiknock agent, for example lead, to mercury in the auxiliary scavenger agent should preferably be at least 3/1. For significant scavenging action of the mercury, this ratio of antiknock metal to mercury should preferably not exceed 200/1. Very satisfactory scavenging action is obtained when the antiknock agent is tetraethyl lead and the weight ratio of Pb/Hg is between 5/1 and 100/1.

Gasolines improved by the addition of mercury-containing scavengers in accordance with the invention may contain other additive materials conventionally employed in commercial gasolines. Such other additives include upper cylinder lubricants and solvent oils for example, solvent oils consisting of hydrocarbon mixtures having a Saybolt viscosity not exceeding about 450 seconds at 100°F., a 50% distillation point above about 350°F. at 10 mm of mercury pressure, and an API gravity between about 18 and about 28. Corrosion inhibitors such as alkyl acid phosphates, amines, amine phosphates and nitrites, dimerized linoleic acid and other carboxylic acids may also be present. Other additives useful in such gasolines include gum inhibitors such as N,N'-di-secondary-butyl-p-phenylene diamine; 2,4-dimethyl-6-tertiary butyl phenol; and 2,6-di-tertiary-butyl-4-methyl phenol. Also useful are anti-icing agents such as isopropanol, hexylene glycol, Carbitol and dimethyl formamide. Such gasolines also conventionally contain dyes such as 1,4-diisopropyl-amino anthraquinone and p-dimethyl-amino-azobenzene; and dye stabilizers such as ethylene diamine. Auxiliary scavengers other than mercury compounds, e.g. tricresyl phosphate, iso-octyl phosphate, or methyl diphenyl phosphate, can also be used in conjunction with the mercury compounds.

The mercury-containing scavengers may be incorporated into such gasolines in a number of different ways, depending upon the particular mercury compound utilized. It is generally preferred to employ gasoline-soluble mercury compounds and to embody those compounds in additive concentrates containing other materials to be added to the fuel.

The exact nature and objects of the invention can best be understood by reference to the following examples:

EXAMPLE 1

Di-n-butyl mercury was added to a commercial premium grade gasoline, containing 3·0 cc. per gallon of tetraethyl lead, 1·0 theory of ethylene dichloride and 0·5 theory of ethylene dibromide, in a concentration of 1·0 gram per gallon. This concentration provided about 0·63 gram of elemental mercury per gallon of gasoline. The base gasoline had the following inspections:

ASTM Distillation	
Initial Boiling Point	106°F.
10% Boiling Point	142°F.
50% Boiling Point	216°F.
90% Boiling Point	291°F.
Final Boiling Point	349°F.
Gravity, °API	56·3
Reid Vapor Pressure, PSI	8·2
Sulfur, Wt. %	0·03%
Research Octane No.	101·5
Motor Octane No.	89
Tetraethyl Lead, cc/gal. (as Ethyl Fluid)	3·0

Intimate mixing of the mercury compound into the base fuel produced a homogeneous fuel composition.

In order to determine the effectiveness of the mercury-containing scavenger in the gasoline composition prepared as described above, tests were carried out wherein a 1957 Cadillac automobile having a standard V–8 engine of 10·0 to 1 compression ratio was first operated on the base gasoline containing no mercury until an equilibrium octane requirement had been attained and was then operated on the same base gasoline modified by the addition of 1 gram of di-n-butyl mercury per gallon as previously described. Prior to the start of the test, the engine was cleaned of all deposits, overhauled and equipped with new spark plugs. Conventional commercial lubricants were used in the car throughout the test.

The test was carried out under conditions designed to closely simulate average city-suburban driving. The car was operated an average of about 185 miles per day at speeds between idle and about 50 miles per hour, averaging about 25 miles per hour. At the beginning of the test, the noise-free octane requirement of the engine was determined by operating it upon commercial reference fuels of known octane quality in accordance with the standard Uniontown procedure. It was found that the clean engine had a no-noise octane requirement of 89·2 Research Octane Number. Similar determinations were made at approximately 1000 mile intervals until a total of 6000 miles had been accumulated. At this point the results of successive tests showed that the engine had built up sufficient combustion chamber deposits to reach the equilibrium octane requirement and that further operation on the base fuel would not result in further significant octane requirement increases. The engine after 6000 miles operation on the base gasoline had a no-noise octane requirement of 96·4 Research Octane Number. The spark knock octane requirement was 93·0 and the surface ignition octane requirement was 96·4.

Following the attainment of equilibrium

no-noise octane requirement on the base gasoline as described above, and without any cleaning of the combustion chamber, the car was operated on the same gasoline containing 1·0 gram of di-n-butyl mercury per gallon until equilibrium was again attained. As before, determinations were made at periodic intervals to ascertain the engine octane requirements. It was found that the use of the mercurial additive reduced the spark knock octane requirement from a Research Octane Number of 93·0 down to 91·5 and reduced the surface ignition octane requirement from a value of 96·4 down to 91·5. The no-noise octane requirement of the engine after operation on the base gasoline containing mercury additive was about 4·9 Research Octane Numbers lower than that obtained with the same gasoline in the absence of the additive and was only about 2 octane numbers higher than that of the clean engine containing no deposits at all. The surprising effectiveness of the additive for reducing surface ignition and spark knock is thus demonstrated.

During this same test, the effect of the additive on spark plug fouling was also determined by measuring the extent to which spark plug misfiring occurred. The actual number of misfires was counted by means of an electronic misfire counter which detects the radio frequency energy waves produced by the arcing of each spark plug in the engine and marks each time such an arc fails to occur. At the start of the test, the clean plugs failed to fire only 0·2% of the time. After equilibrium octane requirements had been attained with the base fuel containing no mercury additive, after about 6000 miles of operation on the base fuel, it was found that the plugs were misfiring an average of 37% of the time, indicating that very severe spark plug fouling had occurred. Without any cleaning of the plugs or combustion chamber, the engine was continued in service with a fuel containing di-n-butyl mercury. After 5500 miles operation on the fuel containing 1 gm. of di-n-butyl mercury per gallon, spark plug misfiring was found to be occurring only 9% of the time. This clearly shows the beneficial effect of the mercury additives on spark plug fouling.

A further determination made during the course of the test described above involved the collection and weighing of the deposits formed in the combustion chambers of the engine. It was found that the total amount of deposits present after over 10,000 miles operation was only about $\frac{1}{3}$ of the amount accumulated during a similar period of operation on the base gasoline containing no mercury additive. No traces of mercury in the engine and no adverse effects upon exhaust valves could be detected. From this it can be seen that the scavengers of the invention are remarkably effective for preventing the formation of deposits in the combustion chambers of gasoline engines and do not suffer from the disadvantages which have characterized other materials used for similar purposes in the past.

EXAMPLE 2

Tests similar to those described in the preceding example were carried out using a number of different automobiles having compression ratios of 10·0 : 1 or higher. As in Example 1, the cars were first operated using a base gasoline containing 3 cc. per gallon of tetraethyl lead, 1·0 theory of ethylene dichloride and 0·5 theory of ethylene dibromide at a rate of about 400 miles per day until equilibrium octane requirements had been attained. The base gasoline used had properties similar to those of the fuel described in Example 1. The same cars were then operated on the same fuels modified by the addition thereto of various amounts of di-n-butyl mercury. The driving regimen was identical for all cars. The results of determinations of the equilibrium octane requirements of the engines on the base fuels and on the same fuels containing the di-n-butyl mercury are shown below.

1	2	3	4	5	6	7		
CAR	$Hg(C4H_9)_2$ Concentration in Gms/Gal. for Cols. 5 & 7	Equilibrium (2) Spark Knock Octane Requirement			Equilibrium (3) Surface Ignition Requirement		Octane Requirement Decrease Effected by Hg	
		Clean Engine	After Base (1) Fuel	After Base (1) + Hg	After Base (1) Fuel	After Base (1) + Hg	Spark Knock	Surface Ignition
Buick 1957	1·0	94·1	99·0	96·5	101·1	98·3	2·5	2·8
Buick 1959	0·5	93·2	97·6	96·8	98·9	96·4	0·8	2·5
Cadillac 1957	1·0	88·9	94·9	93·0	96·4	93·3	1·9	3·1
Cadillac 1959	0·5	93·5	96·2	94·8	99·9	95·9	1·4	4·0
Cadillac 1959	0·1	91·5	97·8	95·5	98·9	95·0	2·3	3·9
Chrysler 1959	0·1	95·7	98·7	97·2	99·9	97·7	1·5	2·2
Ford 1958	0·1	91·8	94·2	93·7	95·0	92·5	0·5	2·5
Lincoln 1959	0·1	94·5	99·8	96·7	99·9	96·3	3·1	3·6
Oldsmobile 1958(4)	1·0	89·7	92·5	90·8	95·0	91·6	1·7	3·4

(The words "Buick", "Cadillac", "Chrysler", "Ford" and "Oldsmobile" are Registered Trade Marks)

(1) Contains 3 cc. TEL/gal.

(2) Based on average of every rating after equilibrium had been reached at 3000 miles on base fuel and average of every rating after equilibrium had been reached at 2000 miles on fuel containing Hg at concentration described.

(3) Based on highest rating on base fuel and the average of two or three of the last ratings on Hg fuel in which S.I. occurred.

(4) This car was run first on Hg fuel followed by base fuel. All other cars were run on base fuel and then on Hg fuel.

From the above data it can be seen that use of the mercury-containing scavenger resulted in reductions in spark knock equilibrium octane requirement of up to 3·1 octane numbers and reductions in surface ignition equilibrium octane requirement of as much as 4·0 octane numbers. These data corroborate the results shown in Example 1 and clearly indicate the surprising effectiveness of mercury-containing scavengers for reducing the adverse effects of combustion chamber deposits in gasoline engines. These reductions are particularly significant at the high levels of 92·5 to 101·1 octane numbers in these cars of very high compression ratio.

Example 3

The absence of effect of the mercury-containing scavengers of the invention upon the octane quality of gasolines to which they are added is shown by tests carried out by measuring the Research and Motor Octane Numbers of a leaded gasoline with and without the mercury-containing scavenger. The gasoline employed in these tests was a commercial leaded gasoline containing 3·0 cc. per gallon of tetraethyl lead, 1·0 theory of ethylene dichloride and 0·5 theory of ethylene dibromide. It had the following inspections:

ASTM Distillation	
Initial Boiling Point	102°F.
10% Boiling Point	138°F.
50% Boiling Point	248°F.
90% Boiling Point	320°F.
Final Boiling Point	365°F.
Gravity, °API	48·4
Reid Vapor Pressure, PSI	7·3
Tetraethyl lead, cc/gal. Added as Ethyl Fluid	3·0
Research Octane Number	106
Motor Octane Number	96

The Research Octane Number of this gasoline was determined by the standard ASTM Research Method, Test Procedure D908–51, which is described in the 1952 Edition of "ASTM Manual of Engine Test Methods for Rating Fuels". The Motor Octane Number was determined by the standard ASTM Motor Method, Test Procedure D357 which is set forth in the 1953 Edition of "ASTM Manual of Engine Test Methods for Rating Fuels". Di-n-butyl mercury was then added to the gasoline in a concentration of 5·0 grams per gallon and the octane numbers of the fuel were redetermined. It was found that the Research and Motor Octane Numbers of the gasoline were unchanged by the addition. These results indicate that despite the high concentrations used, the mercury-containing scavenger did not destroy the effect of the tetraethyl lead antiknock in the gasoline and at the same time did not itself behave as an antiknock agent.

Example 4

In order to determine the effect of the mercury-containing scavenger agents of the invention upon other properties of gasolines to which they may be added, stability and compatibility tests were carried out using di-n-butyl mercury in a typical commercial premium grade gasoline, containing conventional additives including a small amount of a phosphate such as tri-octyl phosphate or tricresyl phosphate. Stability tests and analyses were first run on the base gasoline without any mercury scavenger. Di-n-butyl mercury was then added to the fuel in a concentration of 1·0 gram per gallon. After two months' storage in ordinary steel tanks, the gasoline was again analyzed and subjected to stability tests. The results of these tests are shown in the following table.

Effect of Mercury-Containing Scavengers on Gasoline Stability

	Base Gasoline	Base Gasoline + 1·0 Gm/Gal. of Di-n-Butyl Mercury After 60 Days Storage
Tetraethyl Lead Content, cc/gal.	2·77	2·72
Chlorine Content, Wt. %	0·04	0·04
Phosphorus Content Gms/100 ml.	0·001	0·001
Hexylene Glycol Content, Vol. %	0·11	0·11
Di-n-Butyl Mercury Content, Gms/gal.	0	0·97
Peroxide Content, Milliequivalents of oxygen per liter of sample	0·10	0·04
Gum, Mg/100 ml. (ASTM D. 381)	2·2	3·0
ASTM Breakdown Time, Minutes (A.S.T.M. D/525)	>400	>400

From the foregoing data it can be seen that the presence of the di-n-butyl mercury had no perceptible effect upon the stability of the gasoline and the mercury compound did not

interact with other additives present in the fuel. Tests of a similar gasoline with and without 1·0 gram per gallon of di-n-butyl mercury showed that the mercury compound neither increased nor decreased the rusting tendency of the gasoline.

EXAMPLE 5

The following compositions are representative of gasolines to be used in accordance with the present invention:

A. An aviation gasoline with initial boiling point of 105°F., mid-boiling point of 210°F. and final boiling point of 315°F. is blended with 4 cc. of tetraethyl lead per gallon, the tetraethyl lead being in the form of "Aviation Mix" fluid containing 1 theory of ethylene dibromide, and with 0·002 gm. of mercury diphenyl per gallon and is used to operate a Continental aviation engine with direct injection. (The word "Continental" is a Registered Trade Mark).

B. A highly aromatic motor gasoline, containing 40% of catalytically hydroformed naphtha and having 425°F. end point and 9 lbs. per sq. in. Reid vapor pressure, is blended with 2 cc. of tetraethyl lead per gallon, the tetraethyl lead being in the form of "Motor Mix" fluid containing 1 theory of ethylene dichloride and 0·5 theory of ethylene dibromide, and with 0·01 gm. of mercury methyl isooctyl per gallon and is used to operate a Cadillac engine with carburetion.

C. A highly paraffinic gasoline, substantially sulfur-free, containing 65% butylene alkylate and having 395°F. end-point and 11 lbs. per sq. in. Reid vapor pressure, is blended with 5 cc. of iron carbonyl per gallon and with 0·25 gm. of mercury petroleum sulfonate per gallon and is used for breaking in a Chevrolet engine with direct injection.

WHAT WE CLAIM IS:

1. A method for preventing the formation of adherent deposits in the combustion chambers of a gasoline engine operated on a fuel containing a metal-containing antiknock agent which comprises introducing into the combustion chambers of the engine a mercury-containing substance in proportions sufficient to provide up to 2·0 gms. of mercury per gallon of gasoline burned.

2. A method as claimed in claim 1 wherein the mercury-containing substance is a mercury-alkyl compound in which the alkyl groups contain from 1 to 8 carbon atoms.

3. A method as claimed in claim 2 wherein the mercury alkyl compounds is di-n-butyl mercury.

4. A method as claimed in any of claims 1 to 3 wherein the mercury-containing compound is introduced into the combustion chambers with the gasoline.

5. A gasoline composition comprising a lead alkyl antiknock agent in proportions of from 1·0 to 6·0 c.c.s. per gallon, from 0·5 to 3·0 theories of a halohydrocarbon scavenger agent and a mercury alkyl compound, wherein the alkyl groups contain from 1 to 8 carbon atoms, in proportions sufficient to provide up to 2·0 gms. of mercury per gallon of gasoline.

6. A gasoline composition as claimed in claim 5 wherein the mercury alkyl compound is present in proportions sufficient to provide from 0·0015 to 1·5 gms. of mercury per gallon of gasoline.

7. A gasoline composition as claimed in claim 6 wherein the mercury alkyl compound is present in proportions sufficient to provide from 0·01 to 1·0 gm. of mercury per gallon of gasoline.

8. A gasoline composition as claimed in any of claims 5 to 7 wherein the mercury alkyl compound is di-n-butyl mercury.

9. A gasoline composition as claimed in any of claims 5 to 8 wherein the lead alkyl antiknock agent is lead tetraethyl and the ratio of lead to mercury in the gasoline is between 3 to 1 and 200 to 1.

10. A gasoline composition as claimed in claim 9 wherein the ratio of lead to mercury in the gasoline is between 5 to 1 and 100 to 1.

11. A method as claimed in claim 1 substantially as hereinbefore described in the Examples.

12. A composition as claimed in claim 5 substantially as hereinbefore described in the Examples.

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